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MBE-grown CaF_2 nanostructures on Si(001)

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Abstract. Atomic force microscopy and reflection high energy electron diffraction have been used to study initial stages of CaF_2 epitaxial growth and formation of nanostructures on Si(001). A variety of nanostructures has been observed including ultra-thin two-dimensional layers at 750°C, quasi one-dimensional wires at 650°C and well-ordered dots of almost equal size at lower growth temperatures. An attempt has been made to understand the influence of the growth parameters on the orientation and shape of the resulting nanostructures.

Introduction

Fabrication of new solid state nanostructures is known to offer unique opportunities in creation of new micro-, opto- and magnetoelectronic devices. However, traditional lithographic procedure is very difficult to use in forming nanostructures with characteristic size of less than 10 nm, that are necessary for quantum well devices operating at room temperature. Therefore self-assembled nanostructures are very attractive. One of suitable candidates to be used as a lithographic mask is CaF_2. This compound is chemically inert and well matched to Si lattice. When deposited on Si it causes no intermixing at CaF_2/Si interface. Recently it has been demonstrated that fabrication of CaF_2 nanostructures is possible both on Si(001) [1] and Si(111) [2] substrates. In this work, we applied reflection high energy electron diffraction (RHEED) and atomic force microscopy (AFM) to study initial stages of CaF_2 epitaxial growth and formation of epitaxial nanostructures on Si(001) in a wide range of growth conditions.

1. Experimental

Fluoride nanostructures were grown in a custom MBE system. After standard chemical cleaning, Si substrate was transferred into growth chamber and thermally cleaned at 1250°C for ~2 min. Then it was kept at 1000°C for 15 min to flatten the surface. The RHEED pattern of the prepared substrate showed a well pronounced 2×1 superstructure which is characteristic of the clean Si(001) surface. The fluoride was deposited at the rate of 2–3 nm/min from the molecular beam formed by sublimation of single-crystal CaF_2 pieces from an amorphous carbon crucible. The nanostructures were grown at relatively high temperatures (450–750°C) and in most cases after cooling down to room temperature were capped with 10 monolayers (ML) of CaF_2 for protection from humidity and oxidation. The surface morphology was studied out of the MBE system with atomic force microscope produced by NT-MDT (Zelenograd, Russia). The microscope was operated in the tapping mode at cantilever resonance frequency of 300–400 kHz.

2. Experimental results

It is known that clean Si(001) surface is dimerized to show 2×1 reconstruction. On a vicinal surface the dimerization changes orientation by 90° on every single atomic step. This results

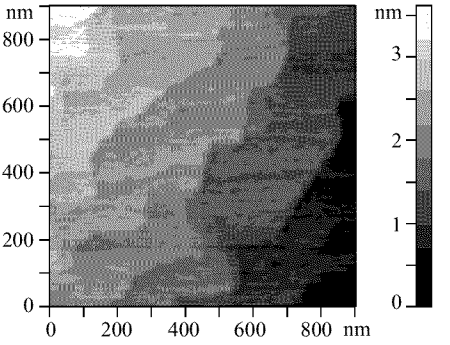

Fig. 1. The surface morphology of Si(001) substrate after the pregrowth treatment.

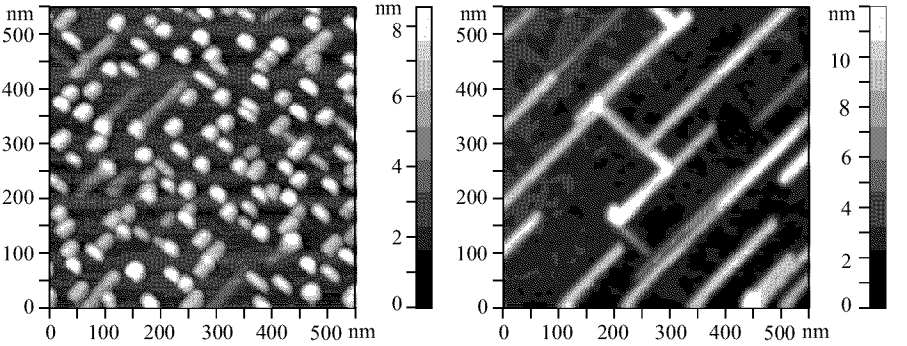

Fig. 2. Surface morphology of Si(001) surface with 1 ML of CaF_2 deposited at (a) 450°C, (b) 550°C.

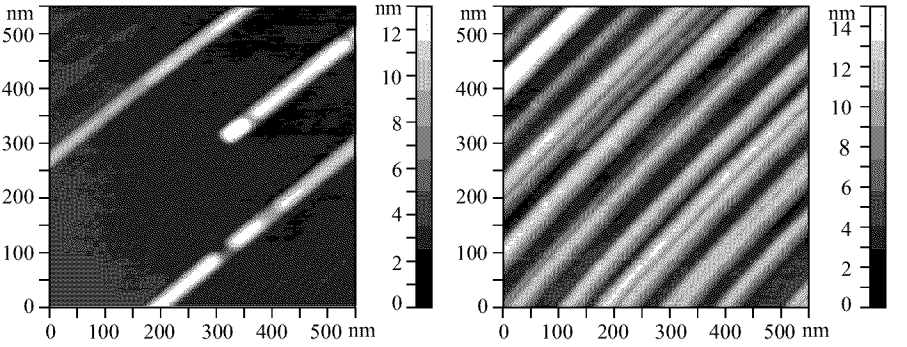

Fig. 3. Surface morphology of Si(001) surface with 1 (a) and 6 (b) ML of CaF_2 deposited at 650°C.

in alternating of 2×1 and 1×2 reconstructions across the surface. Figure 1 shows typical surface morphology of Si(001) substrates which have passed high-temperature cleaning and 1000°C treatment. One can see 100–200 nm wide terraces separated by single atomic steps and step bunches consisting of up to 8 single atomic steps. The surface morphology drastically changes after 1 ML of CaF_2 is deposited on the substrate at 450°C. Figure 2(a) shows domination of 20–40 nm wide rectangular islands 4–8 nm high with the sides parallel to [110] and $[\bar{1}10]$ directions. One can also see several [110]-aligned narrow stripes attached

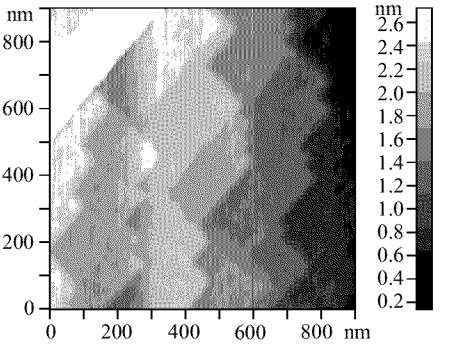

Fig. 4. Surface morphology of Si(001) surface with 6 ML of CaF_2 deposited at 750°C.

to some of the islands. At higher growth temperature (550°C) instead of the rectangular islands we observe series of long wires (Fig. 2(b)). Most of the wires run along [110] direction, however some of them are orthogonal to it. It is noteworthy that the wires never cross each other, but rather form a T-shape joint. Increasing the growth temperature to 650°C, one obtains the structure with even longer [110]-aligned wires (Fig. 3(a)). The wires exceed several microns in length being only 3–8 nm in height. The measured width ~20 nm, however, may be larger than the actual one because of the finite sharpness of the cantilever tip. A much higher density of the wires is observed if CaF_2 coverage is increased up to 6 ML at the same growth temperature (Fig. 3(b)). Further increase of the growth temperature to 750°C at the same coverage (6 ML) leads to a considerable decrease in the wire density. Surface steps of tooth-saw shape with edges parallel to [110] and [1$\bar{1}$0] are clearly observed between the wires (Fig. 4).

3. Discussion and conclusion

Taking into account that the (111) surface has minimal surface energy in the fluorite structure [3], it is natural to suppose that the side facets of the nanostructures shown in Figs. 2–4 are formed by {111} planes. In principle, there are two possible ways to build such a nanostructure. The first one is to form a pyramid or a hut with (100) base and {111} facets. One can expect that such an island will be elastically strained in the interface plane, because the mismatch between CaF_2 and Si lattices is less than 2%. The other possible way of an island growth is with the CaF_2 [110] direction normal to the Si substrate surface. In this case, the lattice mismatch along one of the Si ⟨110⟩ directions is the same as for the pyramid (< 2%), however in the perpendicular direction, the mismatch can exceed 45%. Therefore, one can expect that this type of the islands will be partially or completely relaxed in the direction of their width.

The data presented above as well as in [1, 4] show that at the initial stages of CaF_2 growth on Si(001) the latter type of islands dominate on the surface. Their epitaxial relations (CaF_2 [110] // Si[001], CaF_2[1$\bar{1}$0] // Si[1$\bar{1}$0] for the islands aligned along [1$\bar{1}$0] and CaF_2[1$\bar{1}$0] // Si[001], CaF_2[110] // Si[110] for [110]-aligned islands) are confirmed by both HRTEM measurements [1] and our RHEED observations which showed the patterns similar to the observed in [5] during CaF_2 growth on Si(110). The island nucleation is likely being influenced by surface reconstruction on Si. It is known [6] that diffusion on the 2 × 1 reconstructed Si surface is highly anisotropic. Diffusion is much easier along the rows of dimers than across them. Provided the diffusion length exceeds the terrace width, the most

likely terraces for island nucleation are those where the diffusion prevails along the terrace rather than across it. The reason for this is that the admolecule concentration is higher at the terraces with a longitudinal diffusion. However in the case of short diffusion length (low growth temperature) the nucleation on both types of terraces will be equally probable. It is believed that the island is nucleated with the well-matched CaF_2 [110] direction parallel to the dimer rows on the Si terrace. Once the nucleation occurs the island extends along the well-matched direction keeping constant width along poorly matched CaF_2 [100] direction. An additional reason for the one-dimensional growth is that the diffusion is much easier along the dimer rows. That means that the island orientation is determined at the nucleation stage. At high growth temperature the nucleation occurs at only one sort of reconstructed terraces, leading to the same orientation of all the islands on the surface (Fig. 3, 4). At lower growth temperature both 2×1 and 1×2 terraces are allowed for nucleation which results in growth of both $[1\bar{1}0]$- and [110]-aligned wires (Fig. 2(b)). Due to the lower admolecule diffusion length, these wires are much shorter than the ones grown at higher temperature. Decrease in the wire density with growth temperature (Fig. 3, 4) can be explained by the increase in the rate of fluorine depletion taking place during formation of CaF_2/Si interface. As it was shown in [4] it is accompanied by the transition from the formation of elongated islands, similar to the wires observed in our work, to the two-dimensional lateral growth related to the formation of CaF layer at the interface. This process leads to the rearrangement of the steps which become better ordered (compare Fig. 1 and Fig. 4).

In conclusion, we have shown that strong anisotropy of 2×1 and 1×2 domains on Si(100) surface, as well as the temperature dependence of the interface fluorine depletion rate results in the formation of a variety of CaF_2 nanostructures including quasi-zero-dimensional dots and quasi-one-dimensional wires.

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